

# Surface induced structural disorder in semiconductor nanocrystals observed by XANES

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## INTRODUCTION

The emergence of colloidal methods to prepare high quality inorganic nanocrystals has led to an increasing number of studies of size dependent scaling laws. Due to the finite size of nanocrystals, the structure and composition of their surface may have particular significance for their chemical and physical properties [1]. Nanocrystals have a high surface to volume ratio (a 28Å diameter CdSe particle has 37% of its atoms on the surface), and their thermodynamic, electronic, and chemical properties are influenced by the surface [2, 3]. Thus, in order to comprehend fully the size dependent properties of nanocrystals, it is necessary to determine the structure of the surface. However, the surface structure of semiconductor nanocrystals is not well understood. Techniques such as x-ray diffraction (XRD) and transmission electron microscopy (TEM) that yield much information about the shape and interior structure of nanocrystals are insensitive to the atomic configuration at the surface [4-6]. The TEM image in Fig. 1 shows evidence that nanocrystals are crystalline and faceted, but information about the surface is limited. Furthermore, methods that are used to measure the surface structure for two-dimensional surfaces such as low energy electron diffraction require long-range order.

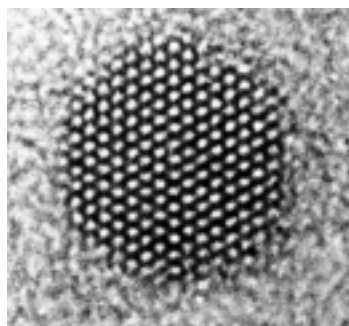


Fig. 1. High resolution TEM image of a CdSe nanocrystal. The scale bar is 50Å.

We use x-ray absorption spectroscopy (XAS) to measure surface atom configurations in nanocrystals. Due to the local nature of the absorption process, XAS does not rely on any long-range order in a sample. The spectrum within 50 eV above the absorption edge (x-ray absorption near edge structure, XANES) is sensitive to the relative arrangement of multiple atoms due to the contribution of multiple scattering effects[7, 8]. From the absorption spectrum one can extract complex information such as bond angles. Here we report that XANES spectra at the In and Cd  $M_{4,5}$  edges of InAs and CdSe nanocrystals show a size dependent broadening which can be interpreted the presence of reconstructions at the surfaces of the nanocrystals.

## EXPERIMENT

CdSe and InAs nanocrystals with a mean diameter ranging from 17-80Å were synthesized according to literature methods [9, 10]. The particles are capped with an organic ligand. High-resolution TEM show crystalline, well separated CdSe (Fig.1) and InAs particles with wurtzite and zincblende lattice fringes, respectively, in agreement with corresponding XRD patterns. Sub-monolayers of particles were deposited onto HF etched Si wafers from toluene solutions. The XANES spectra of the  $M_{4,5}$  edge at 405eV (Cd) and 445eV (In) were measured in total current yield on beamline 6.3.2. The photon energy was calibrated to the F 1s line in  $MgF_2$  (690eV). The linewidth for the 3d core level of both In and Cd is estimated at ~300meV [11] which is the limiting factor in the resolution of the experiment. Note that since we are exciting 3d core

electrons we are mapping the local partial density of states with p-character in the spectra. Therefore, we are *not* exciting into states located at the conduction band edge which are mainly derived from the metal 5s-states, but into higher p-bands that are 2-6eV above the conduction band minimum.

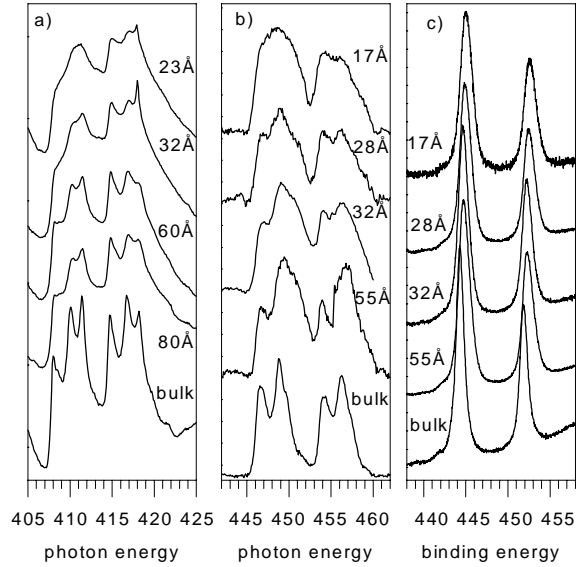


Fig. 2. XANES  $M_{4,5}$  spectra of Cd (a) and In (b) in CdSe and InAs nanocrystals and the bulk materials, nanocrystal diameter in Å. (c) XPS of In 3d core in InAs nanocrystals and bulk.

Fig. 2 shows the absorption edge of the a) Cd and b) In  $M_{4,5}$  edges as a function of size of CdSe and InAs nanocrystals as well as the respective bulk spectra (bottom). As the size of the particle decreases, the spectral features broaden significantly to the point that for the smallest particle (17 Å for InAs) no splitting within spectra is visible anymore. X-ray photoelectron spectroscopy (XPS) of the Cd and In 3d (Fig. 2c) core levels show a slight size-dependent shift to higher binding energies and an increase of the spectral linewidth due to decreased core-hole screening in nanocrystals [12]. However, the magnitude of this effect is negligible compared to the effects seen in the XAS spectra. Therefore, the smearing of the XANES spectrum is not due to

the core level from which the electron is ejected but the environment of the photoelectron in the crystal.

To understand the spectral behavior, we have simulated the In  $M_{4,5}$  edge absorption spectra using a multiple scattering model for XANES spectra, FEFF7 [13]. The particles are modeled as spherical with a layer of In atoms terminating the surface, in accordance with results from XPS [14]. In the simulations, the two outermost layers of In and As atoms are distinguished from those in the interior of the particle by separate calculation of their muffin-tin potential [15]. The absolute energy of the simulated spectra was shifted to match the data at the first spectral feature of bulk (446.5 eV), and the calculation included a broadening of 100 meV to account for the finite experimental resolution and a factor of 300 meV for core hole broadening. Fig. 3 shows simulations (lines) and spectra (dots) of a) InAs bulk, as well as b) 28 Å (441 atoms) and c) 17 Å (99 atoms) diameter InAs nanocrystals using bulk lattice parameters. In agreement with the experiment, the simulated bulk spectrum shows features at 446.5 eV and 449 eV, though it introduces a spurious peak around 460 eV. For the nanocrystals, the simulation predicts similar results with

a slight broadening of the features at 446.5 eV and 449 eV as the size of the nanocrystal is decreased. However, the degree of broadening in the calculated spectra is much smaller than observed in the experimental data. Apparently, if the nanocrystal has uniform bulk bond lengths, the spectra of the

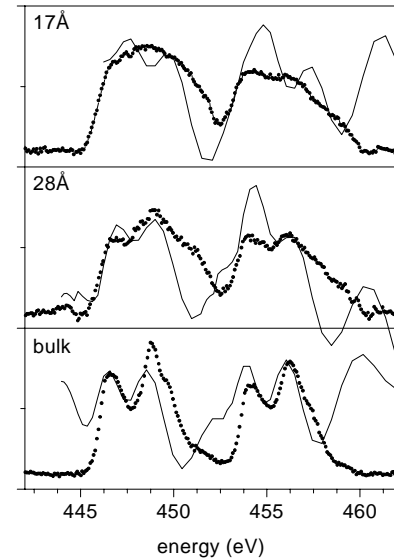


Fig. 3. In  $M_{4,5}$  spectra of InAs nanocrystals and bulk (dots) with FEFF7 simulations (lines) for nanocrystals assuming bulk lattice constants.

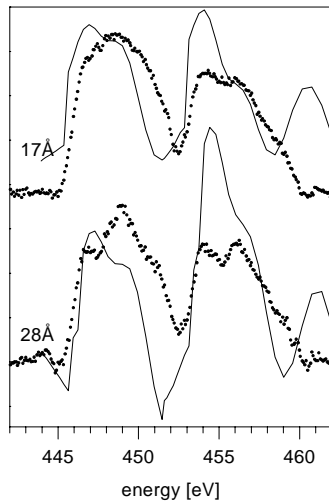


Fig. 4.  $M_{4,5}$  spectra for 17Å and 28Å nanocrystals (dots) and FEFF7 simulations including a surface reconstruction.

smaller particles is not reproduced. Thus, the observed broadening does not arise solely from the finite number of coherent scatterers.

When a reconstruction of the surface into the calculation for spherical 17Å and 28Å InAs nanocrystals (Fig. 4) we observe a broadening of the simulated spectrum comparable to the experiment. We assume a relaxation of the outermost In layer by  $-0.85\text{Å}$  (inwards) and the next As layer by  $+0.39\text{Å}$  (outwards). This is similar to results from calculations for III-V bulk semiconductors [16]. For the (110) surface of zincblende III-V and  $(10\bar{1}0)$  surface of (II-VI) wurtzite semiconductors this type of reconstructions conserves the nearest neighbor bond length but changes angles [17]. Note that in nanocrystals this surface relaxation changes the bond lengths at the outermost surface layers. This increases the number of distinct photoelectron scattering paths in a nanocrystal, yielding a broadening of the XANES spectra in the simulations. However, the experimental broadening may not only be due to a structural

rearrangement of exclusively the two outermost layers as assumed here. It is very probable that the reconstruction is quite complex, where geometries deviate from the bulk values throughout the particle, the largest displacements at the surface. However, lacking an appropriate model to account for such rearrangements, we only state here that the observed broadening of XANES spectra can be related to structural disorder within the nanocrystals, which is believed to be largely due to atomic displacements at the surface.

Other possible sources for the broadening effects have been systematically studied. We simulated spectra for an unreconstructed 17Å nanocrystal with a) a capping of the outermost In layer with P atoms and b) a slightly elliptical shape shown in Fig. 5. The surface capping with P atoms models the experimental situation that the outermost In layer is covered by a disordered layer of ligands (tri-n-octylphosphine) as confirmed by XPS [14]. Since scattering scales as  $Z^2$  (the atomic number) the P atoms are a negligible contribution to the spectrum compared to As or In. An elliptical particle shape (aspect ratio 1.1) which has been observed [3, 6] increases the number of scattering paths due to the symmetry reduction from a sphere, which should in principle lead to a broadening of the XANES spectra. However, this contribution is insignificant compared to the experimental result. Quantum size effects convoluted with the finite size distribution of the nanocrystals can also be excluded. We simulated the effects of a size distribution with 10% width on the x-ray absorption spectrum of 17Å InAs nanocrystals [18]. The bulk spectrum was convoluted with a Gaussian of a width of 100 meV representing the conduction band shifts corresponding to the size distribution. The result (not shown) exhibits an insignificant amount of broadening of the spectrum relative to the experiment. We conclude that structural disorder in small InAs and CdSe nanocrystals is the major factor in the broadening of the XANES spectra at the In and Cd  $M_{4,5}$  edge.

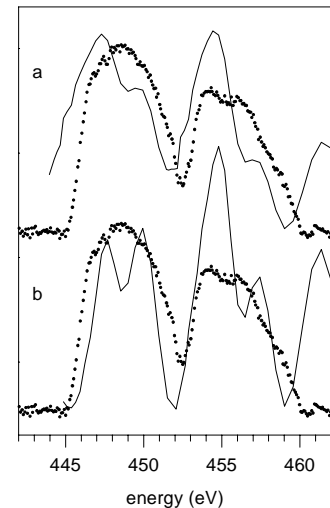


Fig. 5. FEFF7 simulations of an unreconstructed 17Å nanocrystal with (a) P on the surface and (b) an aspect ratio of 1.1.

However, as may be expected for a single bulk-derived reconstruction of the outermost surface layers, it is still not in quantitative agreement with the experiment. The simulation of XANES in larger nanocrystals requires substantial improvement of the multiple scattering calculations. Also, the simultaneous presence of multiple faces, each with different reconstructions, must be accounted for in the models. Further experiments for nanocrystals with different surface stabilizations might provide enough information on the nature of the reconstruction. The nanocrystals can be stripped of their surfactant and epitaxial shells of related semiconductors can be grown onto the cores (e.g. InAs coated with CdS). These surface modifications will provide additional checks on the complex surface reconstructions of the semiconductor nanocrystals.

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